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TENSOR CONCEPTS IN ELECTRONIC STRUCTURE THEORY: APPLICATION TO SELF-CONSISTENT FIELD METHODS AND ELECTRON CORRELATION TECHNIQUES

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1 Extended Abstract

The purpose of this tutorial is to discuss the fundamental role that tensor concepts play in treating electronic structure problems in nonorthogonal basis sets. In almost every well-defined electronic structure method, an approximate Schrödinger equation is solved in a truncated subspace of the full many-electron Hilbert space. The solution may be viewed as a vector in this subspace, which can be represented in any convenient basis. Textbooks favor orthogonal functions, for simplicity, but in real life a basis of spatially localized nonorthogonal functions, such as atomic orbitals, is by far the most natural choice. This is because in a local representation, sparsity in operator matrices emerges naturally on characteristic length scales. Often the process of orthogonalization destroys locality of orbitals, particularly for unoccupied orbitals.

Unfortunately, in conventional presentations of electronic structure theory, the introduction of nonorthogonality greatly complicates the working equations. Indeed, it looks as if the underlying equations are altered by the use of a nonorthogonal basis set. In fact, this is of course not the case, and tensor analysis makes this clear, and at the same time allows insights that are not obvious otherwise. This talk will discuss several aspects of the use of tensor concepts in electronic structure theory, with relevance both to density functional theory (DFT) calculations, as well as wavefunction-based electron correlation methods. Two papers [1,2] and a book chapter [3] will cover parts of the tutorial that have already been published. The last part of the tutorial will involve material that is not yet published, concerning high order electron correlation methods.

We shall begin with an overview of elementary tensor concepts [1,3], and illustrate their use in self-consistent field (SCF) theories, such as density functional theory (DFT). The main interest is in casting the SCF problem in such a way that all known matrix elements and all variables to be solved for are represented in a local nonorthogonal basis. Such a representation is important in the context of developing linear scaling SCF methods. We discuss critical issues in the use of gradient methods to minimize such functions [1], and contrast several strategies for achieving linear scaling.

The second part of the tutorial will introduce the uses of tensors to simplify the treatment of nonorthogonal functions within wavefunction-based theories of electron correlation. The basic theory for this part of the talk is already available [2], and will be reviewed from an elementary perspective. Tensor constructs are

used to express all invariances inherent in many-electron theory. This is useful in the first instance for permitting the use of arbitrary sets of nonorthogonal or even linearly dependent functions within electron correlation methods. All that matters is the space spanned by the functions.

One area where the additional generality afforded by the use of nonorthogonal functions is useful is in so-called local models of electron correlation. The classic local correlation method is the Pulay-Szabo approach, which has also been greatly extended by Schtz and Werner (see their contributions to this meeting). It uses nonorthogonal virtual functions, and orthogonal occupied functions. We shall show that rational alternative models for local electron correlation satisfying all criteria of a theoretical model chemistry can be conveniently developed entirely with atom-centered nonorthogonal functions. These models involve atomic truncations that produce inherently smooth potential energy surfaces, and require no input beyond specification of the atomic positions and a single particle basis set. The physical significance of these models, their computational requirements, and their quantitative performance will be discussed.

The final part of the tutorial concerns the general problem of correcting truncated coupled cluster wavefunctions for neglected electron correlation effects. The main existing approach to this problem is the very widely used CCSD(T) method. We shall discuss an alternative approach to obtaining non-iterative corrections to truncated coupled cluster methods that appears to have substantial promise. It involves two sets of single particle functions which are nonorthogonal amongst themselves, and are therefore most naturally treated in the framework of tensor algebra.

References

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